TOWARDS THE DEVELOPMENT OF DEFECT-FREE GaN SUBSTRATES: DEFECT CONTROL IN HETERO-EPITAXIALLY GROWN GaN BY NEW BUFFER LAYER DESIGN

Joachim Krüger, Yihwan Kim, Sudhir Subramanya, and Eicke R.Weber (P.I.)

Department of Materials Science and Mineral Engineering
University of California at Berkeley
Berkeley, California 94720-1760, USA

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ABSTRACT

This study analyzes the influence of the low-temperature grown GaN buffer layer on the properties of the GaN layer for thin film growth on sapphire. Considerable efforts have already been spent during the course of the past ten years on the optimization of buffer layers and progress in the arena has made the realization of commercially available GaN-based opto-electronic devices.

We introduce the *stoichiometry* of the buffer layer as a new parameter determining the quality of the subsequently grown GaN layer. Adequate design of the growth conditions allows to grow GaN films of significantly improved crystalline and electrical quality. The achieved electron mobilities are among the best ever reported for MBE grown GaN films on sapphire. We further establish a qualitative growth model explaining the observed phenomena by the stoichioemtry-dependent ability of the buffer layer to relax stress during growth.

In a second closely-related matter, the main causes of stress in hetero-epitaxially grown GaN are - for the first time - analyzed by measuring the temperature dependence of the GaN bandgap in reference to a lifted-off GaN film. Surprisingly, the observed temperature dependence of stress between 0 and 600 K can not be explained under the mere assumption of thermally induced stress caused by the mismatch of the thermal expansion coefficients.

INTRODUCTION

The availability of suitable substrate materials is a key requirement for thin film growth of the technologically and scientifically promising III-V semiconductor GaN. Due to the lack of large scale homo-epitaxial templates GaN is usually grown on substrates differing in the lattice constant and thermal expansion coefficient. The resulting stress causes a huge density of crystalline defects currently severely hindering the development of high-performance devices. The advent of GaN-based opto-electronic devices in the early 90's has only become possible by the introduction of low-temperature grown GaN buffer layers.

In a previous study [Kru1], we have analyzed the main parameters determining stress in the main layer. Further, we have introduced a new concept to control and even take advantage of these stress components to grow material of desired quality [Kie2]. For instance, stress in the film during growth can alter the surface mobility of Ga ad-atoms and consequently the growth mode, thereby vastly influencing the surface morphology [Fuj1]. Since defects tend to replicate in the subsequently grown GaN layer, it is of crucial importance to control stress (and thereby the amount of defects) in the GaN substrate.

EXPERIMENTAL

The nominally undoped, Si-, or Mg-doped GaN films were grown using a rebuilt Riber 1000 chamber with activated nitrogen species being provided by a Constricted Glow Discharge Plasma Source developed at LBNL. The buffer layer were grown at 500°C on the nitridated sapphire substrate, and the main layer gwere deposited at 725°C. The typical main layer thickness was (0.5 - 1.0) μm. All main layers were grown under the same conditions, only the buffer layer growth parameter were varied. For further growth details, see ref. [Kim1].

In selected cases the buffer layer thickness was determined by cross-sectional electron microscopy (TEM) or Rutherford Backscattering (RBS), all other values was calculated from the buffer layer growth rate and time.

The 4K photoluminescence was excited by a 50mW HeCd laser, diffracted by a 0.85m double grating monochromator and detected by a UV-sensitive photo-multiplier. The a- and c-lattice parameters were measured with a Siemens D-5000 diffractometer equipped with a four bounce Ge monochromator. In selected cases, the stress values determined by photo luminescence were confirmed by Raman and room temperature absorption spectroscopy.

The surface morphology was observed by atomic force microscopy (AFM) in the contact mode. Hall effect measurements were taken at room temperature using the Van-der-Pauw configuration.

RESULTS

a) Analysis of relationship between GaN buffer layer composition and main layer quality

From our previous studies it is already known that GaN films may be under stress *at the growth temperature* depending on the stoichiometry of the growing main layer. This effect is due to the huge difference in the atomic radii of the two elements, as pointed out in the introductory section. Therefore it is now interesting to study the stoichiometry of the *nucleation layer* has an impact on the main layer's composition. The composition of the low temperature grown GaN buffer layer was changed by varying the nitrogen flow while keeping the Ga source evaporation temperature constant. At the moment, no characterization method is known being capable of determining the exact composition of a GaN layer. By Auger spectroscopy and high-precision X-ray diffraction of the GaN buffer layers, however, we attained first preliminary indications that a change of the III/V flux ratio translates in some fashion into a change of the buffer layer's stoichiometry.

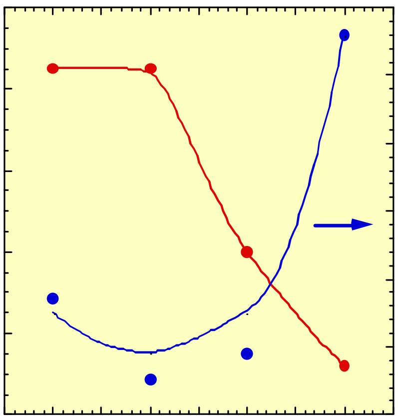

Figure 1: *Hall mobility of the GaN main layer and threading dislocation density as function of the buffer layer's stoichiometry.*

While the surface morphology of the epilayer is not affected by the buffer layer's composition, a very strong effect on the material's structural and electrical properties is found. Fig.1 shows the electron mobility (as measured by Hall effect) for GaN as a function of nitrogen flow during growth of the buffer layer, [Kim2]. Apparently, the maximum mobility was achieved for a Ga-rich buffer layer. In the case of undoped GaN we find an increase from μ = 12 cm^2/Vs to 85 cm^2/Vs, in the case of Si-doped GaN one even realizes an improvement from 78 cm^2/Vs to 250 cm^2/Vs (not shown here). The latter one represents an exceptional good value for a MBE grown film of only 2 µm in thickness! It should be pointed out, however, that the concentration of free carriers stays practically constant for these series, [n] = (3-4) $10^{17}cm^{-3}$. Thus, a conceivable change of the carrier scattering mechanism by a decrease of ionized centers can be excluded. In fact, this increase of the carrier mobility is due to the improvement of the crystalline quality of the epilayers, which is also proved by TEM investigations. Fig. 1 depicts that a decrease of the threading dislocation density as measured by TEM results in an increase of the carrier mobility. This can be understood with the common notion that dislocations act as a scattering center of charged carriers, [Wei1].

This effect is also clearly reflected in the width of the X-ray rocking curves. Generally, the full width at half maximum (FWHM) of the symmetric (002) and of the asymmetric (101) rocking curves are an indication of the

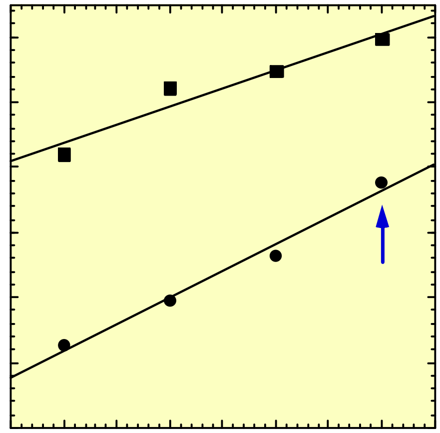

Figure 2: *Amount of residual stress in main layer as function III/V flux ratio during growth of the buffer layer*

crystalline disorder of the out-of-plane and in-plane structures, respectively. Both in-plane and out-of-plane disorders are reduced by a factor of 4 by growing a buffer layer with a larger Ga/N flux ratio. It is also found that there is a good agreement between the threading dislocation density and the FWHM of asymmetric x-ray rocking curves. It is known that asymmetric X-ray rocking curve evaluates a degree of twist between grains and is broadened by threading dislocations, [Hey1, Pon1]

To find an explanation for this peculiar but consistent behavior we have analyzed the buffer layers by various techniques. A change in the buffer layer thickness or surface morphology can be excluded by Rutherford backscattering (RBS) and Atomic Force Microscopy (AFM), respectively.

While the above mentioned parameters of the buffer layer fail to explain the observed phenomena, the varying amount of residual stress (measured at RT) present in the GaN epilayers as shown in Fig. 2 offers a reasonable explanation. Apparently, layers grown on a Ga-rich buffer layer are higher compressively stressed than on N-rich material.

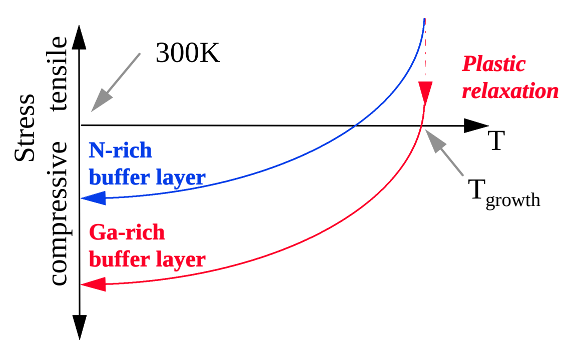

Figure 3: *Sketch of temperature dependence of stress in the GaN main layer for two GaN buffer layers of different stoichiometry.*

We are proposing that a variation in the Ga/N flux ratio changes the buffer layer's composition and, consequently, its plasticity. At the epilayer's growth temperature, it is assumed that the plasticity of the buffer layer is increased with Ga/N flux ratio of the buffer layer. Thus, the coalescence of the growing nucleation islands is improved during the initial growth stage. This process can account for the reduced threading dislocation density of the epilayers grown on Ga-rich buffer layer. Generally, threading dislocations are formed when three-dimensional islands in the early stages of the growth coalesce resulting in out-of-plane and in-plane disorders, [Kap1].

Our model can further explain the difference in residual stress of GaN epilayer at room temperature. As revealed in Fig. 2, the amount of compressive stress on GaN epilayer increases with increasing Ga/N flux ratio of the buffer layer. A similar trend is also observed for the series of Mg doped GaN epilayers. The absolute values of stress are apparently different between Mg-doped GaN and undoped, which may be attributed to the doping, [Kim1]. It is reported that GaN usually grows under tensile stress at the epilayer's growth temperature, [Hea1]. The difference in thermal expansion is expected to generate an increase of compressive stress upon post-growth cooling. Therefore, epilayers under stress-free conditions at the growth temperature should be more compressively stressed at room temperature than epilayers grown under tensile stress at the growth temperature, as shown in a schematic diagram of Fig. 3. It is argued that a "soft" Ga-rich GaN buffer layer provides near stress-free conditions for the growth of the epilayer. These arguments are analogous to the explanation of the improved quality of GaN when grown on the layer with "soft" character such as a thin silicon layer on insulator substrates [Cao1] and InN buffer layer [Kac1].

b) Analysis of thermal dependence of biaxial stress in hetero-epitaxially grown GaN

As pointed out in the preceeding sections, the exact causes of stress in hetero-epitaxially grown GaN are unknown. Based upon the linear thermal expansion (TEC) coefficients for GaN ($\alpha = 5.59 \times 10^{-6}$/K), for sapphire ($\alpha = 7.5 \times 10^{-6}$/K), and for SiC ($\alpha = 4.2 \times 10^{-6}$/K), all values are measured at room temperature [Lan1], GaN crystals grown on sapphire should be compressively stressed, whereas crystals grown on SiC should be under tensile stress. Up to this point, however, no publication is able to *quantitatively* explain the influence of the substrate on the amount of stress in the GaN main layer. Due to experimental constraints, it is unfortunately difficult to determine stress *in-situ* during growth and subsequent cooling down.

Stress can be most conveniently determined by photoluminescence at cryogenic temperatures. It is known to shift the PL transition of the donor bound exciton (DX) spectrum by 27meV/GPa with the stress-free position located at 3.467 eV, [Kie1]. Besides being subject to built-in stress at a given temperature, near band gap transitions are also temperature dependent, as they follow the temperature dependence of the bandgap. For the last 25 years, numerous publications have attempted to determine and explain the bandgap temperature dependence of hetero-epitaxially grown GaN. The huge differences in the observed dependencies have been ascribed to various material and growth parameters, such as the growth method, post-growth cooling down rate, sample thickness, to name a few. None of these publications, however, is in the position to sort out one particular parameter and to describe or even explain its influence on the GaN bandgap temperature dependence.

This study now has taken an entirely new approach to the described problems. Removal of the sapphire substrate via a laser-assisted liftoff technique [Won1] provides a reference sample which allows studying *exclusively* the temperature dependence of stress. For the first time, it is therefore possible to distinguish between intrinsic and material specific effects of the band gap temperature dependence on the one hand and stress effects caused by the thermal mismatch between sapphire substrate and GaN layer on the other hand.

The laser lift-off technique originally developed by Wong and Sands [Won1] for MOCVD grown films has been extended to the usage of HVPE grown GaN. HVPE grown GaN films are shown to exhibit a stress gradient of about 1 GPa measured from the interface side to the layer's top side, fig. 4. This huge amount of stress is known to result in considerable wafer bending currently preventing any subsequent lithographic processing steps. Upon lift-off, however, the HVPE layer is found to be completely stress relaxed, i.e. the layer doesn't exhibit any stress gradient anymore [Kru2], fig 4.

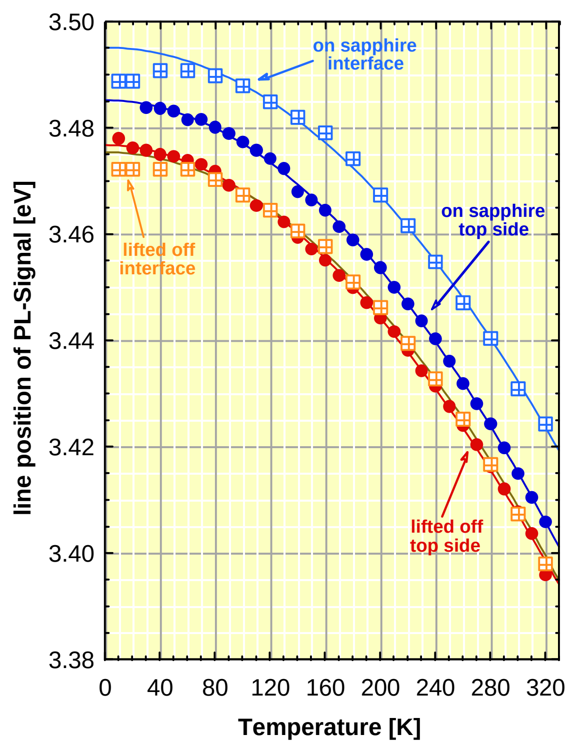

Figure 4: *GaN bandgap (as determined by photo-luminescence) for a HVPE-grown GaN film. Data points in blue are taken for material still attached to its sapphire substrate. Luminescence was excited either from the top or from the sapphire side. Red data points are taken for the respective free-standing material.*

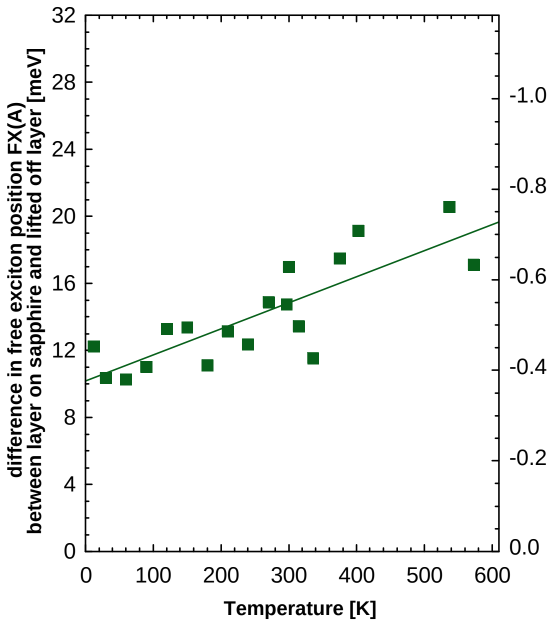

Figure 5: *Difference in energetic position of the free exciton A between GaN film on sapphire and the free-standing reference sample.*

It is illustrative to analyze the temperature dependence of the difference in the band gap energy between the sample on sapphire and its respective free-standing reference sample (see figure 6) eliminating material specific effects. Apparently, with decreasing temperature also the difference decreases indicating that the GaN layer is *less compressively* stressed. This finding is surprising and in contradiction to the prevailing understanding in the literature. Since the TEC of sapphire is higher than the TEC of GaN, the GaN main layer should be *increasingly compressively* stressed with decreasing temperature – provided that the TECs are temperature-independent. Consequently, the energetic difference between the PL spectrum of the free-standing layer and the layer still attached to the substrate should increase. Strikingly, the opposite tendency is experimentally observed.

Two possible explanations for this finding should be discussed: First, the variation of stress in GaN grown on sapphire in the respective temperature range is not governed by the thermal mismatch between GaN and sapphire. The second and more likely cause is given by the uncertainty of published thermal expansion coefficients for both sapphire and GaN, [Lan1, Les1]. The reported values differ by a factor of two, even when only values taken at room temperature are compared. The TEC temperature dependence is even less known so that one may speculate that an unanticipated temperature behavior of these parameters might be responsible for the here observed stress dependence.

The results of this work, however, strongly suggest to measure the temperature dependence of the a and c lattice parameter by X-ray diffraction. Preliminary studies are already available [Hei1, Les1], but their results are not conclusive yet. Measurements of a lifted-off GaN film will provide the best basis for a solid data collection.

SUMMARY

In this study we have explored for the first the impact of the buffer layer composition of the quailty of the subsequently grown GaN main layer. A thorough analysis of residual stress in these layers has let to the postulation of a new model claiming that a Ga-rich buffer layer allows to efficiently relax stress at the growth temperature and leads to material of superior quality.

Further, for the first time the temperature dependence of stress in GaN grown on sapphire has been analyzed (in respect to the reference sample lifted off from its substrate). The obtained results are in striking contradiction to theoretical predictions mostly like due to the inadequacy of published values for the thermal expansion coefficients for both GaN and sapphire.

The results obtained in this study demonstrate the importance of an in-depth analysis of stress and strain in order to develop the use of HVPE grown GaN as a substrate material for GaN homoepitaxy.

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